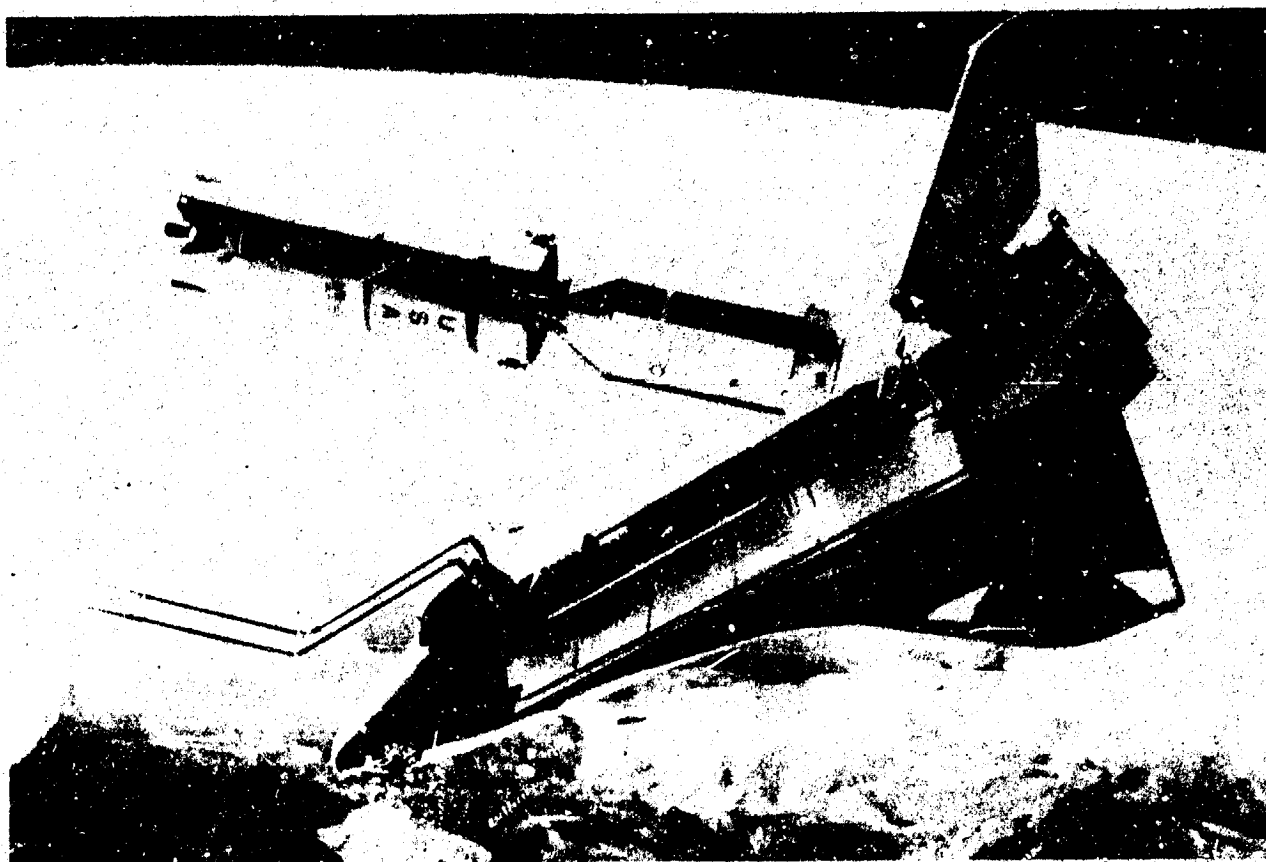


**MONOPROPELLANT ENGINE INVESTIGATION
FOR SPACE SHUTTLE
REACTION CONTROL SYSTEM**

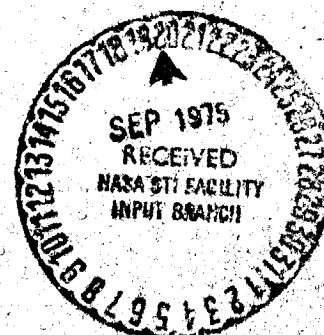
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FINAL REPORT
75-R-460
Volume III



Improvement of Metal Foam for Catalyst Retention

Rocket Research Corporation
Redmond, Washington

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ABSTRACT

The retention of granular catalyst in a metal foam matrix has been demonstrated to greatly increase the life capability of hydrazine monopropellant reactors. Since nickel foam used in previous tests has been found to become degraded after long-term exposure, a program was undertaken (Task VI of Contract NAS8-28950) to study the cause of degradation, and to develop metal foams of improved durability, using laboratory-size comparatively small samples. The results of this Task VI effort are presented in this document, Volume III of the final report. The most durable foam developed under Task VI was a rhodium-coated nickel foam. An all-platinum foam was found to be incompatible in a hot ammonia (hydrazine) environment. It is recommended to scale up the manufacturing process for the improved foam to produce samples sufficiently large for Space Shuttle APU gas generator testing.

The work described herein was conducted by Dr. Eckart W. Schmidt, manager, chemical research, with the assistance of G. S. Fairfull and D. M. Gates, chemists, and A. R. Fields, research chemist.

1.0 INTRODUCTION

Rocket Research Corporation has demonstrated several novel methods for improving performance of propulsion systems by the use of metal foams. These methods included the use of metal foams in high burning rate solid propellants (References 1 and 2), hybrid high energy propellants (References 3 and 4), monolithic catalyst beds (Reference 5), and composite beds with granular catalyst (Reference 6). The incorporation of a metal foam matrix into the gas generator for the Space Shuttle Auxiliary Power Unit (APU) has resulted in a demonstrated life capability of more than 20 missions (Reference 7) and, more recently, up to 40 missions.

Even though these tests have demonstrated a significant improvement in the state-of-the-art, it has been found that the metal foam suffers damage as a result of long-term exposure to the high-temperature, high-turbulence, erosive and nitriding environment in a hydrazine reactor. Thus, further improvements in life capability of the Space Shuttle APU gas generator would be possible if a more durable foam were available. The objective of Task VI of Contract NAS8-28950 was to study the cause of nickel foam degradation, to develop a more durable metal foam, and to test its properties in small-scale laboratory tests.

2.0 STUDY OF NICKEL FOAM DEGRADATION

Numerous nickel foam samples were studied before and after test firing in hydrazine reactors to investigate the mechanism of nickel foam degradation. The objective of this study was to identify the mechanism of foam degradation. Once the degradation mechanism is understood, corrective action can be taken more efficiently to improve the life of the foam.

The foam samples investigated herein were obtained from Space Shuttle APU gas generators, such as the pressure-modulated and the pulse-modulated development units, and the NASA-JSC test. In each of the tests at least 20 missions had been simulated to different duty cycles. The mission characteristics of the tests to which the foam samples were subjected are summarized in Table 2-1.

2.1 PHOTOGRAPHIC DOCUMENTATION

The close-up photographs shown in this paragraph serve to illustrate the type of damage observed with the various foam samples.

2.1.1 Technology Reactor – Pulse-Modulated Test

The appearance of a foam hemicylinder removed from the inner bed following the pulse-modulated test is shown in Figure 2-1. Several parts broke off from the foam during the attempt to remove it from the reactor. The foam was very brittle and not as ductile as initially. The half-moon shaped caps at the ends were in good shape, whereas maximum wear had occurred in the center of the sample where it was in contact with the two Rigmesh injector elements.

The foam previously removed from the pressure-modulated test was in similar condition.

2.1.2 Technology Reactor – NASA-JSC Test

Following the pulse-modulated test at RRC, the technology reactor was refurbished with a different catalyst bed arrangement under Task IVA and delivered to NASA for testing at the Johnson Space Center. The catalyst arrangement differed from that of previous tests in that a 10 pore/inch instead of a 20 pore/inch foam was used to retain the catalyst. Both the lower and the upper bed were filled with 14- to 18-mesh catalyst. The loading efficiency was only 79.94 percent, which is lower than the loading efficiency typically achieved with 25- to 30-mesh catalyst in 20 pore/inch foam (86 percent).

When inspecting the foam after disassembling the reactor, it was found to be severely worn, in particular in the center portion where it faced the injector elements. A comparison of the 10 pore/inch foam elements before and after firing is shown in Figure 2-2. The foam also was very brittle and had lost its ductility as a result of exposure to the hydrazine reactor environment.

Table 2-1
PROPERTIES AND FIRING HISTORY OF NICKEL FOAM SAMPLES

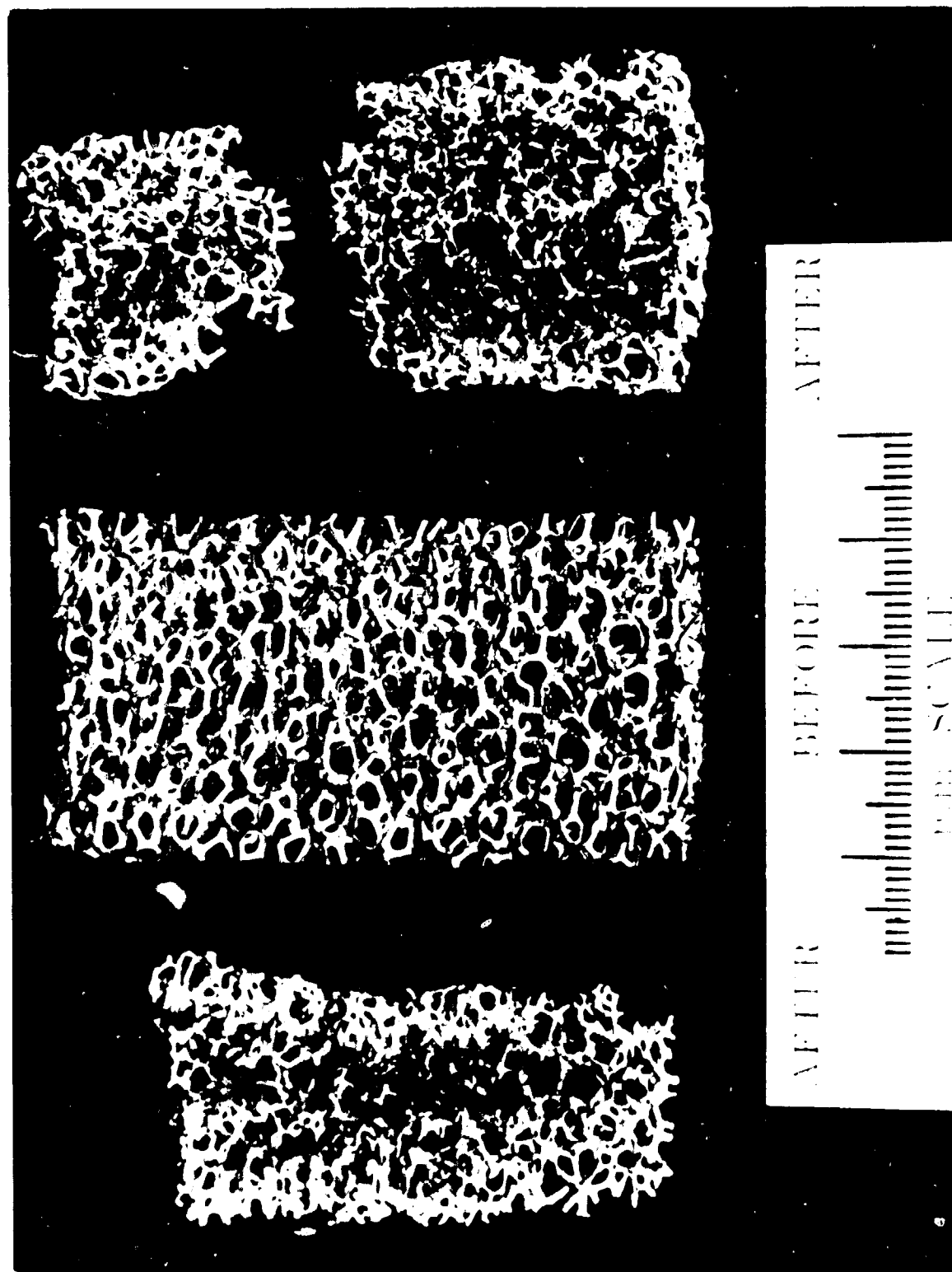
Sample Number	Firing History			Equivalent Total Impulse Delivered lbf-sec	Pre-Test Foam		Post Test Foam		Remarks
	Number of Pulses	On Time (hours)	Propellant (lbs)		Density %	Weight g	Weight g	Weight Loss %	
A1 A2	342,500	9.25	9,600	2,250,000	3.0 2.9	5.48 5.22	9.43	11.9	Technology program Pulse mode test
222A* 111B*	347,087	9.4	8,700	2,100,000	3.2 4.2	5.79 7.77	12.28	9.5	NASA-JSC test

*10 pore/inch foam

GAS GENERATOR FOAM STRUCTURE, VIEW FROM DOWNSTREAM SIDE



10 PORE/INCH NICKEL FOAM BEFORE AND AFTER TESTING AT NASA-JSC. VIEW FROM INJECTOR SIDE



A close-up view, Figure 2-3, shows rounded ligaments. The ligament openings, which typically have a triangular cross-section, are almost closed in several areas by metal which was bent toward the center of the hollow ligament. The areas with maximum wear had a shiny appearance as if freshly sandblasted, whereas foam material in the periphery was dull and dark.

2.2 METALLURGICAL EXAMINATION

Numerous pre- and post-firing foam samples have been mounted in epoxy, sectioned and polished for examination under the metallurgical microscope with incident through-the-lens illumination. This technique was used to study the effects of reactor firings as well as to study process variables and effects of laboratory nitriding tests as described in paragraphs 5.1 and 5.2, respectively.

For the mounting of post-fired foam samples, it was found convenient to use transparent epoxy rather than opaque bakelite. The use of transparent epoxy was preferred because it would allow the operator to determine at which level the sample was to be cut prior to polishing. In several cases, more than one cross-section was taken by repeatedly machining and polishing the sample. Each section was documented by photography before proceeding to the next cut.

It was attempted to have at least one triangular cross-section of a ligament cut at a right angle for each photograph. Because the angle under which the ligament is cut can vary anywhere from 0 to 3590, it was not always easy to obtain a triangular cross-section on the first attempt.

Etching with acid was not always necessary for studying pre- and post-firing nickel foams. Even without etching the metal structure it was so significantly different that some conclusions could be drawn based on unetched samples.

A cross-section of unfired nickel foam will be shown first. This photo (Figure 2-4) serves as a baseline for comparison of pre- and post-firing foam. In the pre-test condition, the foam has already undergone the burn-out and the annealing treatments, which tend to expel any entrapped electrolyte or gas residues. In spite of this, the electrodeposit which makes up the foam structure is very porous and makes the foam more susceptible to attack by nitriding gases. The porosity of the nickel electrodeposited from an all-chloride bath could possibly be reduced by additives to the plating bath. However, all commercial brightener additives contain sulfur and the deposit is rich in sulfur. Sulfur contamination has to be avoided because it would poison the Shell 405 catalyst.

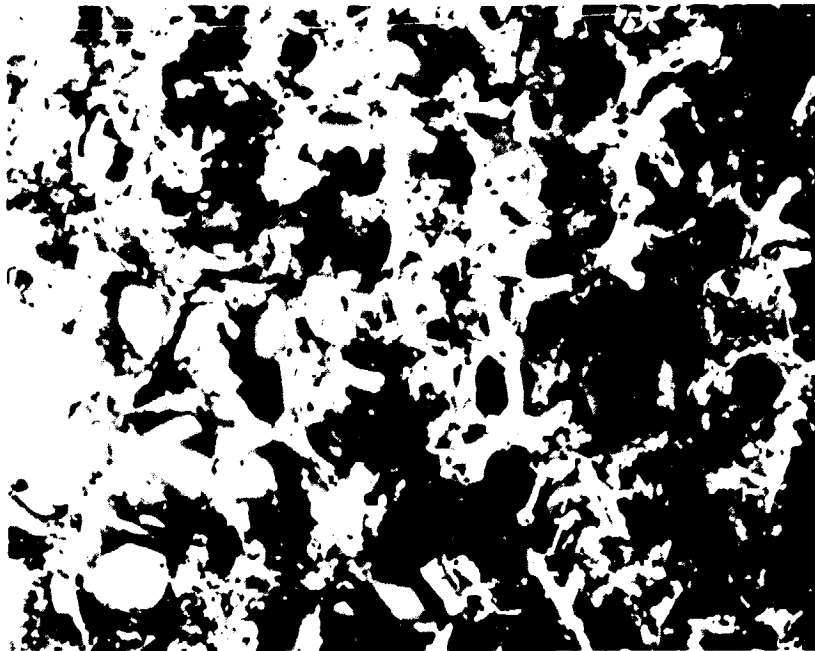
2.2.1 Post Pulse -- Modulated Test Samples

A cross-section of an originally triangular ligament is shown in Figure 2-5. This particular ligament has been flattened by external pressure or impact forces. The porosity is comparable to that observed after 8 hours nitriding in ammonia at 2,000°F.

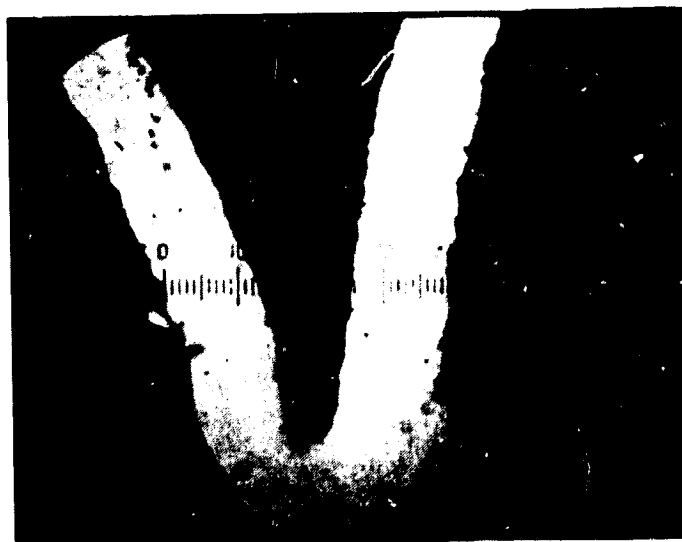
2.2.2 Post NASA-JSC Test Samples

Foam samples taken from an area of maximum wear showed the same porosity as 20 pore/inch foam samples described in the previous paragraph. For a foam of equal density, the ligaments of a

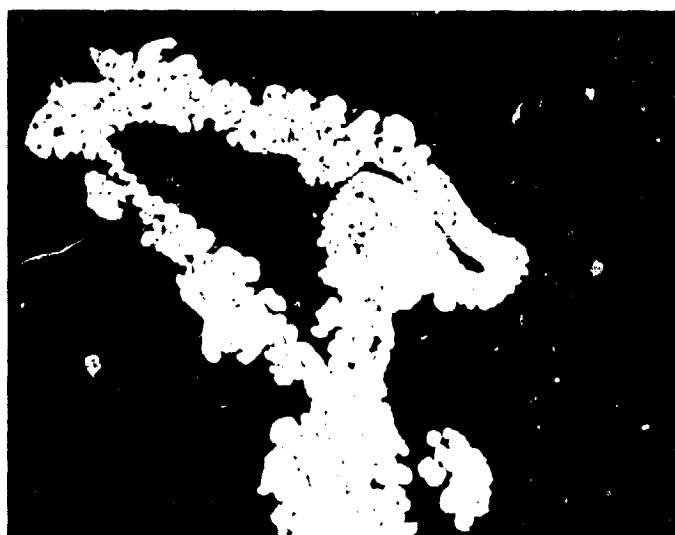
CLOSE-UP PHOTO OF 10 PORE/INCH FOAM,
VIEW FROM INJECTOR SIDE



CROSS-SECTION OF
FOAM LIGAMENT IN UNFIRED NICKEL FOAM, 160X, UNETCHED



CROSS-SECTION OF FLATTENED LIGAMENT,
POST PULSE-MODULATED TEST,
MAGNIFICATION 40X



10 pore/inch foam are larger and have thicker walls. Figure 2-6 shows the cross-section of a ligament which also has collapsed under external forces, allowing opposite walls to touch inside the hollow ligament. Erosion is more pronounced on the outside than on the inside of the ligament.

2.3 ANALYSIS OF DISSOLVED GASES AND CARBON

One sample each of unfired and fired foam has been analyzed for hydrogen, nitrogen, and oxygen by vacuum fusion. In addition to the vacuum fusion test for dissolved gases, the carbon content has been determined by a conductometric method. The results of these tests are summarized in Table 2-2. Whereas no nitrogen could be detected in the unfired sample, the post-firing foam contained 0.012 percent nitrogen. Also, the carbon content increased slightly. The hydrogen and oxygen content remained essentially unchanged.

Table 2-2
C-H-O-N ANALYSIS OF METAL FOAM SAMPLES

Sample	H ppm	O %	N %	C %
Unfired nickel foam	5	0.035	0.003*	0.002
Nickel foam, 10 pore/inch, post test, NASA-JSC	5	0.029	0.012	0.005

*Less than 0.003 (limit of detectability)

The most significant change occurred with the nitrogen concentration. It may be concluded that the damaging mechanism is indeed that of a nitride formation. The number may appear small in terms of weight percent. However, only very little nitrogen is needed to form nitrides along the grain boundaries and weaken the crystal structure.

2.4 ANALYSIS OF CATALYST

Catalyst removed from the APU-GG reactors was analyzed for foreign metal contamination and hydrogen chemisorption. The results are shown in Table 2-3. The nickel is most likely contained as nickel nitride dust which is trapped in the pores of the alumina catalyst carrier. However, some nickel may also have been deposited as nickel vapor from the vaporizing hot nickel foam. Additional studies would be required to identify the nature of nickel contamination.

CROSS-SECTION OF FOAM LIGAMENT
FROM NASA-JSC TEST, MAGNIFICATION 40X



Table 2-3
NICKEL CONTAMINATION OF POST-TEST CATALYST

Test	Propellant Consumed lbs	Catalyst Location	Nickel in Catalyst ppm by Weight	H ₂ Chemisorption μ moles/g
Technology, pressure modulated	12,500	Inner bed	700 to 2,200	103 to 112
		Outer bed	50 to 300	47 to 94
Technology, pulse modulated	9,600	Inner bed	1,080 to 1,170	113
		Outer bed	400 to 440	132
For comparison: Shell 405 unfired			23	135

3.0 LABORATORY TESTS

In addition to investigating foam samples removed from hydrazine reactors, it has been attempted to reproduce the damage observed in hydrazine reactors by subjecting metal foam samples to laboratory tests. These tests were designed to simulate reactor operating conditions as closely as possible. The tests included nitridation tests with ammonia, nitrogen, or hydrazine and attrition tests with nitrogen or ammonia.

3.1 NITRIDATION TESTS

Nitridation tests were conducted with flowing nitrogen or ammonia gas as well as liquid hydrazine. Tests with flowing ammonia in a tube furnace are more easy to conduct, and a significant backlog of materials compatibility data obtained by this method already exists at RRC. Laboratory tests with liquid hydrazine dropping onto a heated test sample are more difficult to conduct and have been performed during this program for the first time.

3.1.1 Nitridation Tests with Ammonia

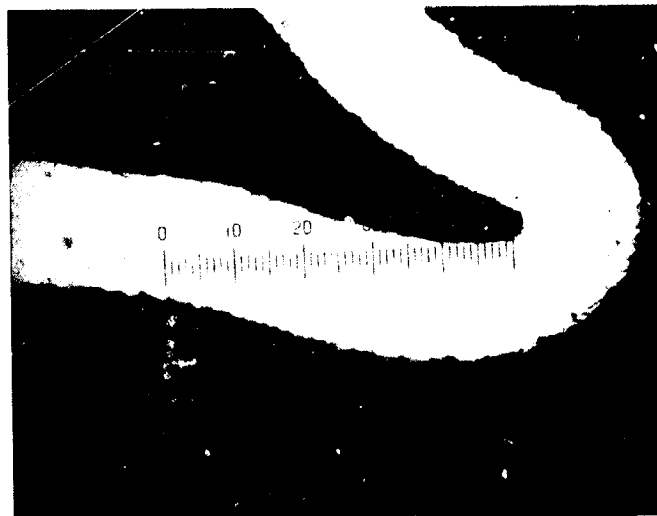
Several series of nitridation tests in flowing ammonia have previously been conducted at RRC (References 8 and 9). Some of these tests were extended to 1,000 hours, others included foam samples similar to the ones now used for the Space Shuttle APU. One test was conducted with repeated monitoring of the degree of ammonia dissociation achieved while the gas passed over the samples. No standard test conditions exist yet, and it is sometimes difficult to compare results obtained in different tests. The main variable is the test temperature and duration. Most previous tests had been conducted at 1,255°K (1,800°F). Upon specific request by NASA, all nitridation tests under this phase of the contract have been conducted at 1,366°K (2,000°F). At this temperature, complete ammonia dissociation occurred over the entire range of practical flow rates, and no ammonia could be detected at the exit of the tube furnace. Even though the emphasis is on nitridation tests at 1,366°K, some results obtained under previous programs at lower temperatures are discussed here for comparison, because they may help to elucidate the degradation mechanism.

A comparison of nickel foam samples previously subjected to 100-hour tests at 922 and 1,144°K (1,200 and 1,600°F) with untreated foam is shown in Figures 3-1A through 3-1C. The higher temperature results in coarser grain structure and the numerous fine pores formed at intermediate temperature coalesce into few larger pores when the temperature is increased to 1,144°K. The photomicrographs show cross-sections of ligament walls of nickel foam cut from the same sample. The corner of a triangular ligament is still visible in the top photo (Figure 3-1A).

The crush strength of nickel foam decreases progressively as nitridation is performed at higher and higher temperatures. Results of crush tests of samples nitrided at 922, 1,144, and 1,366°K are shown in Figure 3-2. The foam yields at lower loads when the nitridation temperature is increased. In the case of the 1,366°K test, the duration of exposure seems to have little effect because a

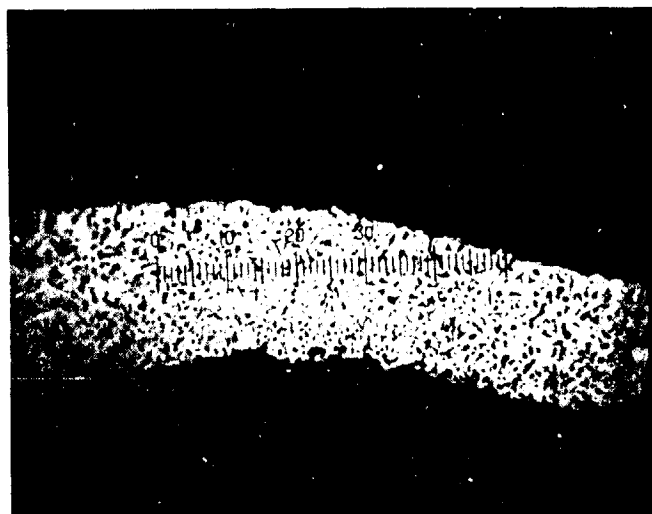
PROGRESSIVE POROSITY FORMATION IN NICKEL FOAM
DUE TO NITRIDATION IN AMMONIA

1 SCALE UNIT 6.25 μm



PRETEST

A



922°K (1,200°F)

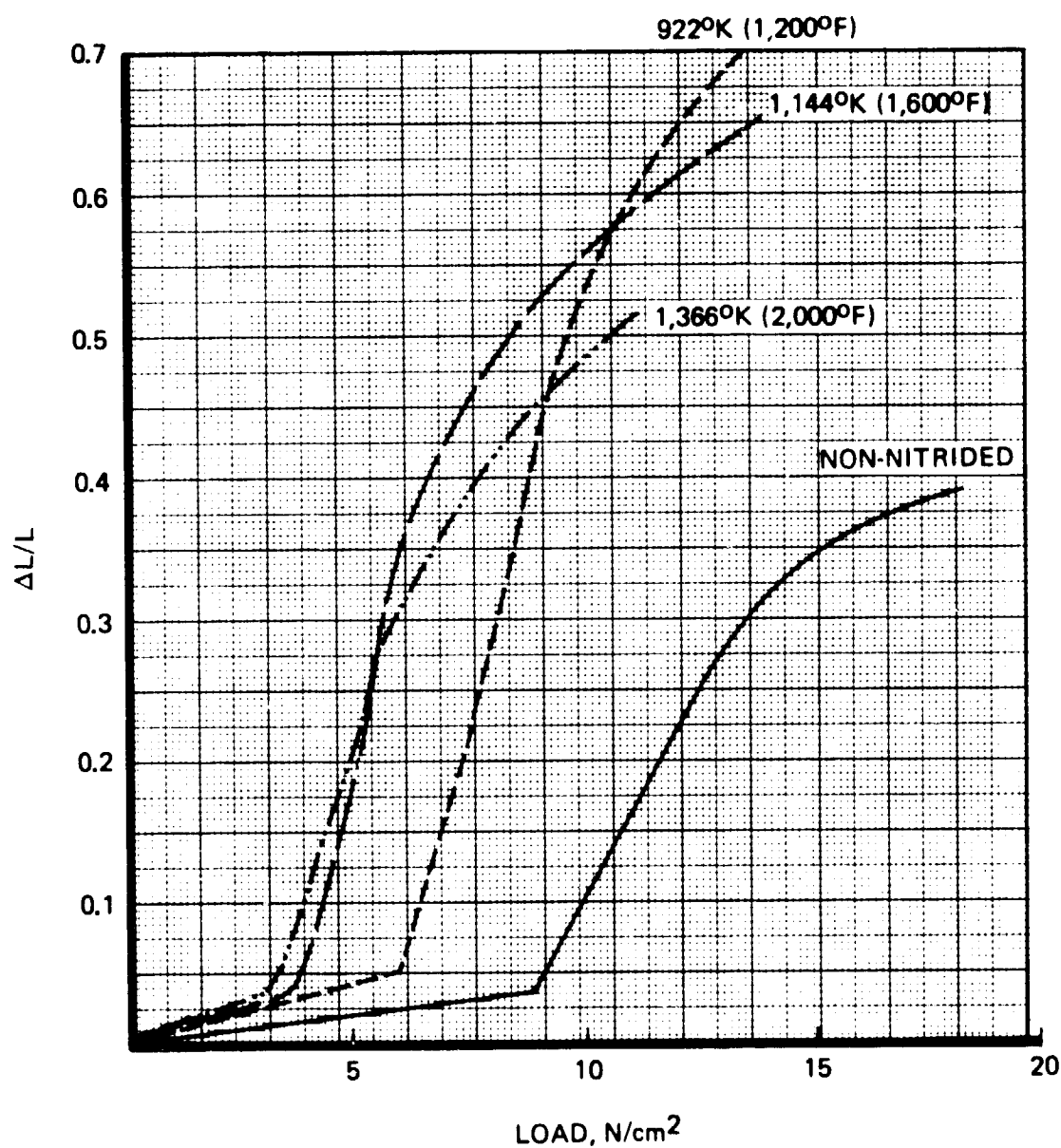
B



1,144°K (1,600°F)

C

**CRUSH STRENGTH OF NICKEL FOAM
AFTER 100-HOUR NITRIDATION IN AMMONIA**



sample exposed for only 8 hours was just as weak as a sample exposed for 100 hours. The most important point in the crush curves shown in Figure 3-2, and similar ones shown in later paragraphs, is the yield point at which the foam starts to deform. Untreated nickel foam with 3 percent density yields at a load of 6 to 8 N/cm², whereas nitrided nickel foam invariably breaks at lower loads. The shape of the crush curves after the sample has started to break shows much scatter and is of little significance.

Several nickel foam samples were subjected to nitridation tests at 1,366°K (2,000°F) for 100 hours during this program. The main objective of these tests was to compare the nitridation resistance of noble-metal coated nickel and pure noble metal foam to that of uncoated nickel foam. Photomicrographs of these samples are therefore shown in paragraph 5.2. Comparing the pores in the 1,366°K (2,000°F) sample with the ones shown in Figure 3-1C, one may conclude that at temperatures above 1,150°K the tendency of the pores to coalesce continues until at 1,366°K no pores are left at all. A sample which had been removed after 8 hours at 1,366°K did show some pores, but these disappeared after 100 hours.

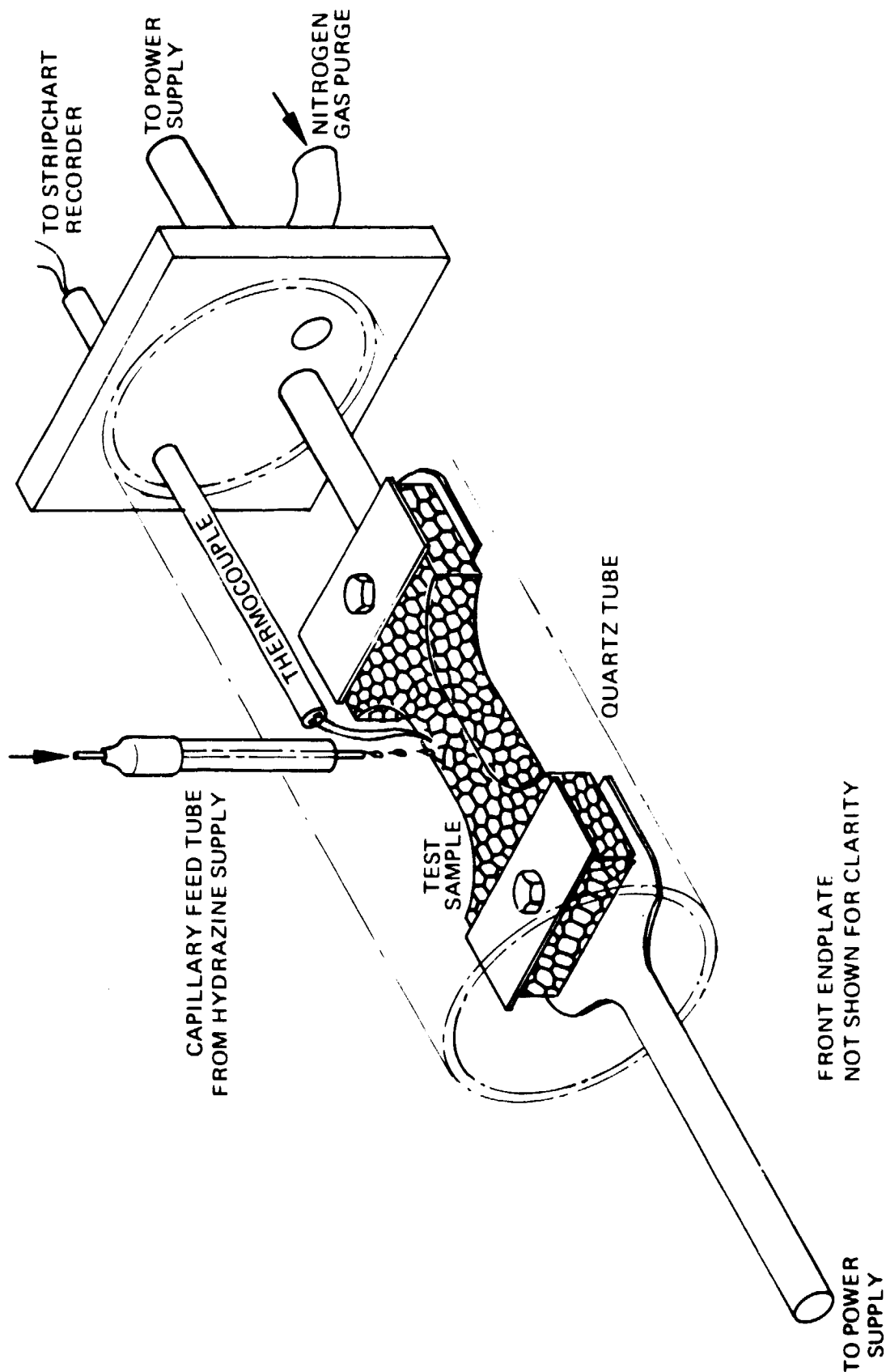
An important question yet to be answered is how porosity relates to mechanical strength of the foam. In spite of the fact that pores had disappeared after 100 hours at 1,366°K, the nitrided nickel foam still was weaker than the untreated samples (see paragraph 5.3). The amount of porosity is therefore not the sole cause for loss of crush strength of the foam.

3.1.2 Nitridation Tests with Hydrazine

In addition to nitridation tests with gaseous ammonia, a limited number of nitridation tests was conducted with liquid hydrazine. The difficulties in conducting these tests are caused by the premature decomposition of hydrazine in the feed tube. It is not advisable to pass a feed tube through a heating jacket when the sample is heated externally, as with the ammonia tests. A unique test setup was therefore designed and built where the samples are heated internally rather than externally. Internal heating is achieved by cutting a dog-bone shaped sample from the foam under test and passing an electrical current through it. The narrow section of the sample heats up very rapidly and can be exposed to dropping liquid hydrazine or flowing ammonia gas.

A schematic of the test setup is shown in Figure 3-3. The dogbone-shaped sample was cut from a foam slab 10 x 25 x 60 mm. The heated test section had a cross-section of 10 x 10 mm and was 25 mm long. The sample was held between two heavy copper bars which served as conductors. The sample was placed into a 200 mm long, 50 mm diameter quartz tube with two aluminum end plates. The endplates contained gas inlet and outlet adaptors, and thermocouple connections in addition to the power feedthrough. The quartz tube had a narrow (3 mm) side arm through which a quartz capillary hydrazine feed tube could be inserted. The end of the quartz capillary was placed in close proximity to the center of the test sample such that the hydrazine would drop on the sample without premature evaporation. A bare-wire thermocouple was tack-welded onto the sample in the vicinity of the impact point. The hydrazine was fed into the capillary from a pressurized stainless steel cylinder through a quick shut-off ball valve, a 5-micron filter, and a needle valve. The hydrazine tank also carried a sightglass to measure the hydrazine supply and calculate the average flow rate.

HYDRAZINE NITRIDATION TEST SETUP



Prior to starting a test, the air in the system was displaced by nitrogen. A nitrogen purge was maintained throughout the test to prevent accumulation of undecomposed hydrazine in the test chamber. A welding transformer served as a power supply. The current was adjusted to result in a sample temperature of $1,366^{\circ}\text{K}$. After all air was displaced from the system, the hydrazine flow was initiated. The flow was adjusted to result in a drip rate of approximately 1 drop every 3 seconds. The liquid hydrazine could be seen boiling in the white hot foam sample for several seconds. The heat transfer was obviously in the film boiling mode because the droplets were supported on a cushion of gas.

The temperature was monitored throughout the tests. In several samples, three thermocouples were attached to the sample to measure the temperature gradient in the axial direction. The temperature differed by 80°K over the 25 mm long test section due to heat loss by conduction to the electrode connections.

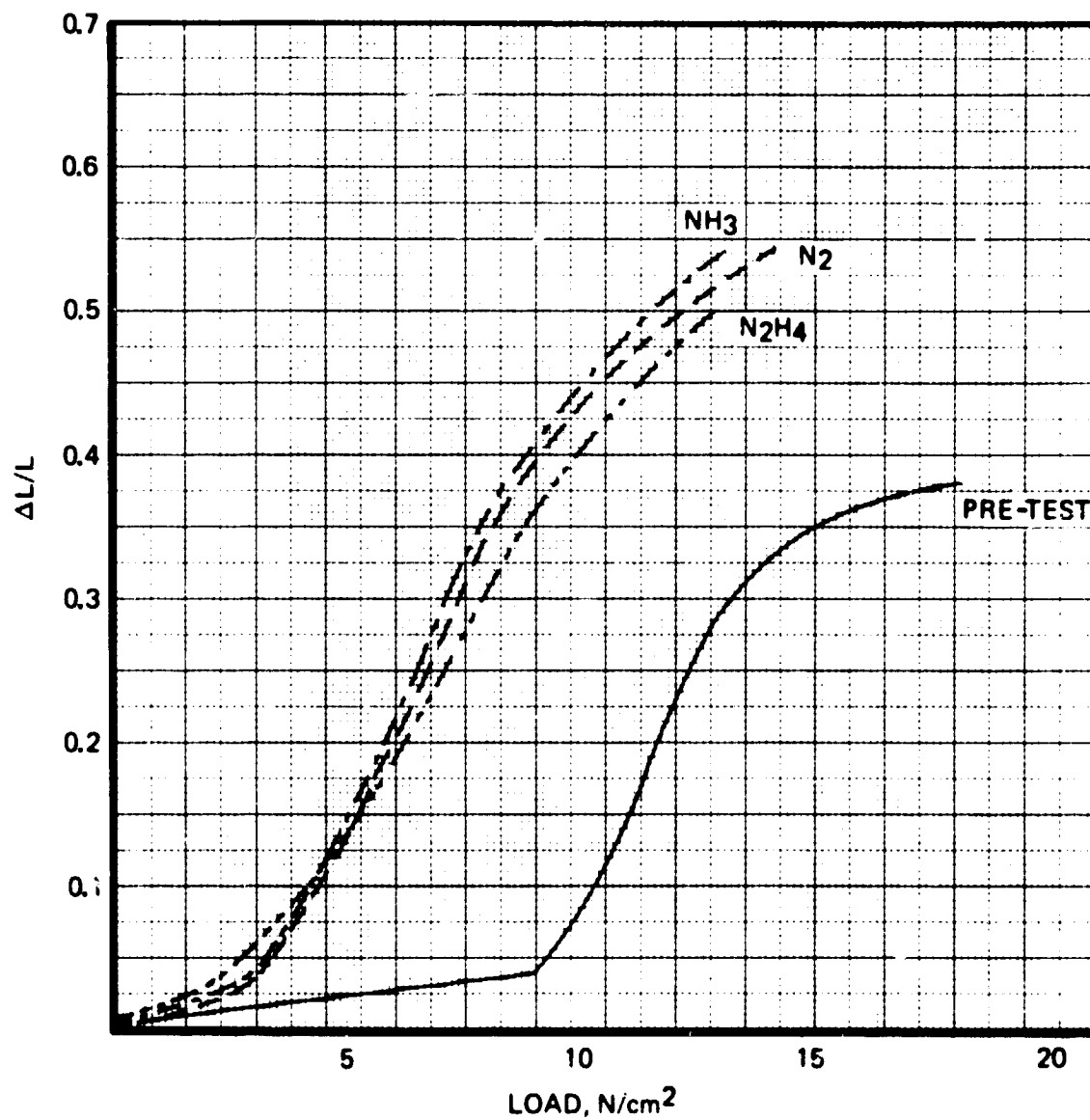
The standard test duration was 8 hours. After this time, the power and the hydrazine flow were turned off and the sample was allowed to cool in nitrogen. The center section was then inspected under the microscope and sectioned for crush test and metallurgical examination. Initially it was attempted to measure weight changes of the samples, but remains of the thermocouple tack weld caused greater weight changes than the nitridation test.

The tests were then repeated with ammonia or nitrogen gas flowing instead of hydrazine dripping. The objective of these tests was to answer the question if hydrazine in the state of decomposition is a more active nitriding agent than ammonia or nitrogen. If this was the case, nitriding tests under ammonia would not represent the true conditions in a hydrazine reactor. Based on the results obtained in this test, the damage pattern of hydrazine and ammonia or nitrogen are identical. As shown in Figure 3-4, the yield point of the three samples coincides. In each case, a significant loss of strength is observed when compared to the non-nitrided specimen (solid curve).

In addition to crush strength tests, several samples were mounted in epoxy and examined under the metallurgical microscope. No difference could be found between samples exposed to dripping hydrazine and samples heated in flowing ammonia. The pores formed in the hydrazine-treated samples after 8 hours at $1,366^{\circ}\text{K}$, or after 10 hours at $1,255^{\circ}\text{K}$ were identical with those formed in an ammonia atmosphere.

One suspected phenomenon which cannot be simulated with gaseous ammonia is that of hydrazine wicking into the interior of hollow ligaments and bursting ligaments by internal pressure resulting from sudden decomposition. The impact area where the hydrazine droplets hit the foam sample was closely investigated for burst and split open ligaments, but none could be found. Based on these test results, it may be concluded that hydrazine does not exert any capillary surface tension forces when it contacts hot foam, because it is immediately separated from the foam by a layer of vapor and decomposition products. Also, visual investigation of post-reactor firing samples has shown that the foam ligaments degrade from external rather than internal forces.

CRUSH STRENGTH OF NICKEL FOAM
BEFORE AND AFTER
8-HOUR TREATMENT AT 1,366°K



3.2 ATTRITION TESTS

The objective of attrition tests was to subject foam samples to the same chemical *and* mechanical environment as in a hydrazine reactor. Without going through the significant expense of designing a hydrazine reactor for this test and using expensive hydrazine as a working fluid, an economical test method was sought which would simulate the reactor environment as closely as possible. It would have been desirable to use a test method which could be set up in a laboratory. However, the requirement of testing with ammonia made it necessary to perform the test in an outside test cell.

Previously, attrition tests have been conducted with a 60° wedge simulating the Space Shuttle RCS monopropellant geometry. During these tests, which were conducted in a chamber with a quartz window, emphasis was placed on survival of the catalyst and no work was done on the foam. The Space Shuttle wedge could not be reused because the bedplates were covered with screens, which make the surface more abrasive than the slotted bedplate design now in use.

A new 180° attrition test fixture was therefore designed which simulated the internal geometry of the Space Shuttle APU GG internal bed more closely. Initially, the fixture resembled the dimensions of the technology program reactor. Following the nitrogen test, the dimensions were changed to agree with those of the flight-type hardware. Prior to the last ammonia test, the bed length was shortened even further to achieve a more concentrated effect.

A photo of the attrition tester prior to the first test is shown in Figure 3-5. The apparatus consisted of a cylindrical bedplate identical to the one used in the technology program. Only one half of the bed space was filled with foam, whereas the lower half was filled with a solid metal hemicylinder. The lower half of the bed was not used for testing. The test fluid was injected through a 12.5 mm diameter tube with radial slots after passing through a preheating coil. Thermocouples could be inserted to measure the gas temperature and the sample temperature. In order to assemble the apparatus, the bedplate was pushed over the foam and the amount of catalyst carrier (calcined RA-1) which could be loaded into the foam was determined. Following this, part of the catalyst carrier was off-loaded again to leave a void of 10 or 20 percent. The two flanges were then bolted together and the assembly was placed into a muffle furnace. The muffle furnace was turned to full power while the test gas was purging to prevent intrusion of air and oxidation of test hardware and test sample. The speed at which the test could be performed was limited by the heat output of the muffle furnace. The duty cycle had to be adjusted to allow a minimum temperature of 1,100°K (1,500°F). The equipment was not suitable to operate at 1,366°K although it would have been desirable to conduct the test at higher temperature.

3.2.1 Attrition Test with Nitrogen

An initial test was performed with nitrogen. The use of nitrogen instead of ammonia is preferred because it can be safely used in an indoor laboratory, and the regulated pressure is independent of the ambient temperature.

The test was started with 0.1-second pulses at a duty cycle of 20 percent. The maximum temperature which could be reached under these conditions was 1,100°K. When the door of the

ATTRITION TEST APPARATUS



muffle furnace was opened for inspection after 12 hours (approximately 85,000 pulses), the Hastelloy-B bed cylinder was found severely damaged by oxidation. Apparently the nitrogen flow rate was not high enough to prevent air from backing up into the muffle furnace. Subsequent tests were therefore conducted with ammonia to maintain a reducing atmosphere inside the muffle furnace at all times.

3.2.2 Attrition Tests with Ammonia

In addition to changing the working fluid from nitrogen to ammonia, the apparatus was changed to use a shorter bed geometry. The new bed cylinder was made from stainless steel CRES 321 and the wall thickness was doubled. The first test allowed a 10 percent void at the beginning of the test. Due to the toxicity and flammability of ammonia and its decomposition products (mainly hydrogen), the experiments had to be relocated to an outside test cell with remote control and remote monitoring. The hot gases escaping from the furnace ignited in air after each pulse. The 0.1-second pulse width at a 5 percent duty cycle would allow a sample temperature of 1,105°K (1,530°F) with an ammonia gas pressure of 340 kN/m² (50 psig). However, during the nighttime the ammonia pressure fell to 200 kN/m² (30 psig) and the temperature rose to 1,227°K (1,750°F) because of the reduced throughput of ammonia (down to 0.13 g/pulse from 0.22 g/pulse). The test was discontinued after 56,000 pulses had been accumulated on the sample. The nickel foam and the catalyst carrier were removed after cooldown. The nickel foam had suffered hardly any degradation and most of the catalyst carrier was recovered. The foam had gained weight by nitridation rather than lost weight by attrition. Post-test sifting of the catalyst carrier showed only 10 percent fines. Some of these fines may have been formed by shrinking rather than attrition. The test conditions were not severe enough and had to be modified for the subsequent tests.

A heating jacket and thermal insulation was wrapped around the ammonia tank and the surge tank to keep the vapor pressure high enough in spite of low ambient temperature. A new foam piece was selected for the next test, and a 20 percent void instead of a 10 percent void was chosen to allow the particles more freedom to move around.

During the test, the ammonia pressure was kept constant at 400 kN/m² and the flow rate was 0.19 g/pulse. Sample temperature was 1,033°K (1,400°F) throughout the test. When the test fixture was opened for inspection after 51,320 pulses, only minimal attrition could be observed on the foam. The catalyst carrier contained 15 percent fines which indicated that the test was more severe than the preceding one.

The test sample size was cut in half for subsequent tests to concentrate the flow on a smaller area and reduce the total flow rate. With a lower flow rate it would be possible to achieve higher temperatures in the muffle furnace. At the same time the remaining injector slots were widened. This resulted in essentially the same total flow rate, but twice the flow rate per foam cross-sectional area (bed loading). After another 52,719 pulses at 1,400°F, the foam sample showed beginning erosion on the outside, but the damage was by far less than what had been observed in hydrazine reactor tests. The attrition tests were discontinued after it became apparent that it was very difficult to reproduce the damage observed in actual reactor firings. Future designs should have the heating element close-coupled to the flanges of the test fixture to improve the rate of heat transfer to the sample and allow testing at higher temperatures.

3.3 MELTING POINT TESTS

The rounded appearance of some of the post-test foam samples suggested that localized melting had occurred. Even though nickel melts at 1,728°K (2,651°F), and temperatures this high have never before been observed in hydrazine reactors, it was of interest to determine the melting point of the nickel foam. The nickel foam is essentially pure nickel and its melting point is expected to be in the vicinity of that of pure nickel. Foam samples were heated in a vacuum bell jar with a graphite heating element while gradually raising the temperature and visually observing the sample for incipient melting. Nickel foam samples melted at 1,672 to 1,705°K, 56 to 23° lower than the literature value. Within the accuracy of the measurement, this must be considered to be close to the melting point of pure nickel. Temperatures this high have never been encountered in hydrazine reactors.

4.0 DEVELOPMENT OF IMPROVED METAL FOAMS

The nickel foam used in the Space Shuttle APU tests to date was selected based on good test results in a 22 N (5 lbf) engine, where the useful lifetime was tripled in comparison to an identical engine without foam (Reference 6). However, the total on-time for that particular duty cycle is short in comparison to that experienced by the APU reactor. Basically, two approaches were considered under Task VI to improve the durability of the foam substrate: coating the nickel foam with a protective material, or replacing the nickel with a more durable foam metal.

4.1 SELECTION OF SAMPLE SIZE

In view of the large expense involved with noble metals and also as the result of difficulties commonly experienced with plating large foam pieces, the sample size for the improved foam development program was chosen small enough to be practical for easy plating and large enough to allow laboratory (not reactor test firing) evaluation tests. The sample size used throughout the Task VI development effort was 50 x 25 x 10 mm. A comparison of this sample size to the size of nickel foam hemicylinders currently prepared for APU GG production is shown in Figure 4-1.

4.2 NOBLE METAL-COATED NICKEL FOAMS

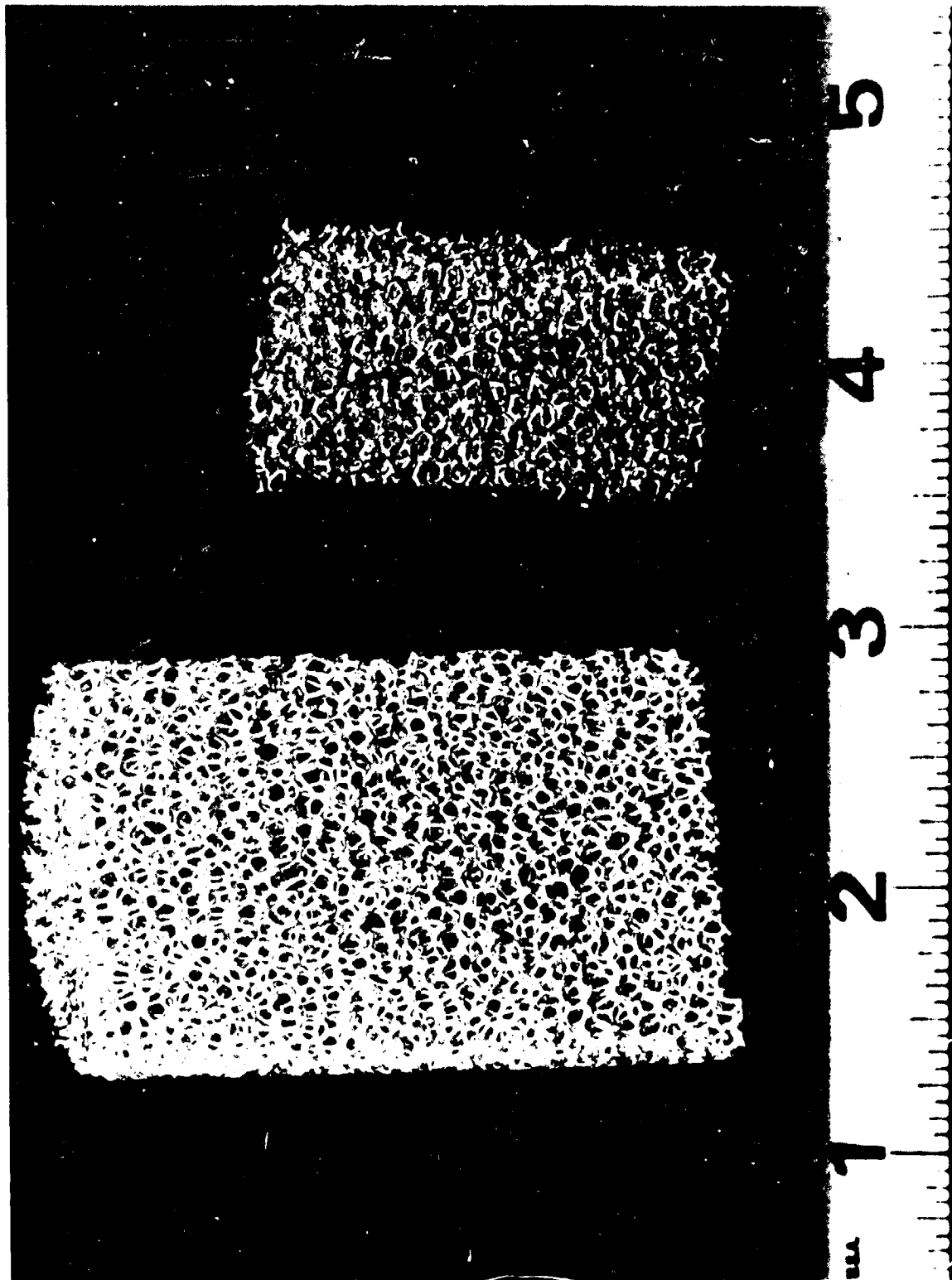
Based on previous experience, it was known that injector and catalyst retention screens could be successfully protected from nitridation in a hydrazine decomposition reactor by a rhodium coating. Therefore, it was obvious that the same technique could be applied to nickel foam as well. In addition to providing chemical protection, the rhodium was also expected to increase surface hardness if abrasion should be a problem.

Previous nitridation tests under Contract NAS 8-28950 (Reference 1) had demonstrated that rhodium plating, also in conjunction with a nickel underplate, provides excellent nitridation protection to Hastelloy-B. The rhodium-coated sample showed the lowest weight gain of all samples tested in ammonia for 30 hours at 1,255°K (1,800°F).

The attack of the nitriding gases on the hollow ligament walls was expected to occur from the outside as well as the inside of the hollow ligaments. A method had to be devised by which the bulk of the foam would be made up of nickel, coated on both sides with rhodium. This was possible by depositing a layer of rhodium first, followed by nickel, and completed by another layer of rhodium on the outside. In this way the nickel would be sandwiched between protective layers of rhodium and, except at machined surfaces, no nickel would be exposed to the decomposition products.

The properties of rhodium coated nickel foam samples and the tests conducted with these samples are summarized in Table 4-1. It is difficult to calculate a true percent density because the weight of the individual layers is not known. The density reported in Table 4-1 is based on the assumption that all of the metal is nickel. Due to the higher specific weight of rhodium, the true density is

SIZE COMPARISON OF PRODUCTION NICKEL FOAM (LEFT) AND DEVELOPMENT NOBLE METAL FOAM (RIGHT)



somewhat lower than the reported number. However, the results show that foam of reproducible density can be prepared in this way. The weight of samples after annealing varies because in some cases small pieces were cut off prior to annealing for microscopic investigations. The results of the tests marked with an X in Table 4-1 will be discussed in Section 5.0.

Table 4-1
SUMMARY OF RHODIUM-COATED NICKEL FOAM SAMPLES

Sample Number	Annealed Weight, g	Density %	Test Performed			Photographs
			Nitridation	Crush-Strength	Metallurgy	
A1/A2		4.08	X	X	X	X
001-4-1	5.276	3.97			X	X
002-4-2	6.624	4.71			X	X
002-4-1	6.669	4.90	X	X		X
002-4-3	5.0151	4.62	X	X	X	X

4.3 ALL-NOBLE METAL FOAMS

The prime objective of this program was to demonstrate the feasibility of manufacturing improved foams. However, it was well recognized that besides feasibility also economic factors will determine the selection of an improved foam. In particular, there is a trade-off between labor and material cost between candidate approaches. It was not within the scope of this contract to conduct a trade-off study in quantitative terms. Additional information would be required before such a trade-off study could be conducted with sufficient confidence to serve as a basis for future decision making.

Selection of noble metals for evaluation as improved metal foams was based on compatibility information known at the beginning of the program. Of the six noble metals (ruthenium, rhodium, palladium, osmium, iridium, and platinum), osmium was eliminated from further consideration due to its volatility in an oxidizing atmosphere. Iridium was not considered further because it is very expensive and it is not available as a commercially formulated plating bath. Palladium and ruthenium are available as commercial plating chemical, but very little is known on their compatibility in a hydrazine reactor environment. Palladium has a very strong affinity to hydrogen and it was suspected that the hydride formation would be associated with a change of mechanical properties. Ruthenium is known to catalyze hydrazine decomposition similar to iridium and would probably be the preferable alternate of the two. Of all metals listed above, rhodium and platinum are the ones with the most extensive backlog of plating experience described in the literature and available from commercial suppliers. These two metals were, therefore, selected for evaluation as all-noble metal foams.

I

Assuming equal performance in a hydrazine decomposition reactor environment, platinum foam would be preferable from a cost standpoint. Rhodium is approximately three times as expensive as platinum. However, due to its lower specific weight (12.4 g/cm^3 as opposed to 21.45 g/cm^3 for platinum), the cost disadvantage for a metal foam of equal density is reduced from 300 to 164 percent.

In addition to noble metals, rhenium has also been considered as a foam metal. Many properties of rhenium are similar to those of tungsten or molybdenum. As such, it is also sensitive to oxidation. Unlike tungsten or molybdenum, it is very ductile and can be electroplated. Commercially formulated plating baths were not available until shortly before this foam improvement program was initiated. Recently, Sel-Rex has discontinued its Rhenex line, and a replacement could not yet be found. Tests with rhenium plating recipes described in the literature were not successful.

4.3.1 All-Platinum Foam

Several all-platinum foam samples have been prepared during this contract and during a previous development program.

Several attempts to prepare all-platinum foam had to be abandoned at early stages in the process. Early attempts to plate platinum directly on electroless nickel had failed due to corrosion of the thin electroless nickel deposit in the platinum plating bath. The electroless nickel was then replaced by electroless palladium, which is more corrosion resistant than nickel. However, the palladium undercoat peeled away in spite of intermediate gold strikes to relieve stress in the platinum coating (Samples 001-4-3 and 002-5-3). It was suspected that the palladium is responsible for this behavior and that the problem is related to hydrogen saturation of the palladium while it is exposed to the electrolyte as a cathode. For this reason, subsequent tests were conducted with electroless nickel protected by a gold strike. Samples 003-1-5 and 003-2-2 were prepared in this way without the flaking problem observed with the previous samples. Figure 4-2 shows a macrophotograph of the platinum foam sample 003-2-2 after 892 minutes of plating. Total density was achieved only after 1,792 minutes of plating. Toward the end of this period the deposit was no longer as smooth as in Figure 4-2. Instead, the deposit became very coarse and was dull in appearance.

4.3.2 All-Rhodium Foam

Several attempts to prepare an all-rhodium foam did not result in the desired product. One sample (002-5-2) plated on electroless palladium with intermediate gold strikes was discontinued after 360 minutes when the metal coating peeled off the substrate and curled in long slivers, some of these curling up in several turns exceeding 360 degrees. This curling is an indication of stress in the deposit, which becomes more pronounced as the thickness of the deposit is increased. Even though the Rhodex rhodium plating bath is advertised as a low-stress process, satisfactory heavy rhodium deposits could not be obtained. The low-stress property is probably true for thin deposits of the order of 100μ inches only.

It was also suspected that the curling could be caused by hydrogen saturation of the palladium. Plating on electroless nickel protected by a gold strike seemed to have helped for the all-platinum

PLATINUM FOAM 003-2-2, MAGNIFICATION 5.3 X



foam (see paragraph 4.4.1). Consequently, the same approach was taken on the all-rhodium foam (Sample 003-3-3). However, the same problem was encountered after only 130 minutes of plating. The next attempt (Sample 003-2-3) used a foam sample which had received an electroplated nickel coating (30 minutes) in addition to the electroless nickel to give it more strength. Again, the nickel was protected by gold before proceeding with the rhodium plating. However, even with the added strength provided by the electroplated nickel, the ligaments burst open after 40 minutes. A heavier nickel underplate (120 minutes) was used in a subsequent sample (003-2-4). This sample seemed mechanically sound when plating was interrupted after 547 minutes in an attempt to burn out the organic and anneal the metal to relieve the stress. This method of stress relief had been recommended by the manufacturer of the Rhodex plating chemicals. However, the structure was not yet strong enough to withstand the forces during the burnout procedure and was damaged in the process. One question which remains unanswered is if it would have been possible to resume plating on the burned and oxidized sample without going through an activating treatment or a pre-plate. It would have been very difficult to remove remaining chemicals from the interior of the then hollow ligaments prior to rhodium plating. The rhodium plating solution is known to be very sensitive to contamination.

The remains of Sample 003-2-4, which contained less than 1 g of rhodium, were used for some compatibility tests described in paragraph 5.1.

4.4 CONVERSION COATINGS

Conversion coatings by chemical vapor deposition (CVD) are frequently used to protect materials in corrosive environments. The prime candidates for conversion coatings on nickel were nickel silicide and nickel boride. The objective of these studies was to deposit a thin uniform layer of silicon or boron on the nickel foam and allow this layer to diffuse into the base metal during subsequent heating in a reducing atmosphere. The silicided or borided nickel foam specimens would then be subjected to nitridation tests. Mechanical properties, such as crush strength, would be measured before and after the nitridation tests to see if the resistance of nickel had improved as the result of applying a protective coating. A literature search was conducted using the DIALOG computer system, but no information regarding nitridation of nickel protected by boriding or siliciding could be found.

Deposition of elementary silicon or boron was achieved by heating the foam specimens in an atmosphere of silicon tetrachloride or boron trichloride in a large excess of hydrogen gas. Because it was initially feared that external heating of metal foam samples in a quartz tube might result in excessive deposition of silicon or boron on the wall of the heated tube, foam samples were resistance-heated internally as described in paragraph 3.1. Ideally, it would have been preferable to heat the samples by microwave induction, but an RF power supply was not available. Resistance heating had one severe shortcoming in that hot spots in the foam sample would result in increased, progressive corrosion, resulting in premature burnout of the overheated zone. Subsequent samples were therefore coated by heating externally in a quartz tube. It was noted that silicon or boron would form preferentially on the nickel foam without excessive deposition on the inside wall of the tube. Apparently the nickel acted as a catalyst for the reduction reaction.

Numerous variables determine the quality of the boron or silicon deposit on the nickel foam: temperature, temperature profile, chloride/hydrogen ratio, flow rate, duration of treatment, and surface condition of the foam. It was not possible to optimize all variables for a given foam dimension. A total of 7 siliciding and 3 boriding tests were conducted as described in Table 4-2. The main problem encountered in all these tests was the uneven distribution of the deposit throughout the foam sample. Both silicon and boron deposits were heavy on the upstream side of the samples but little coating was deposited downstream. Under the given experimental conditions, the samples could not be rotated during the process to achieve more uniform deposition.

Another problem encountered during CVD coating tests was corrosion of the foam matrix by the silicon or boron chlorides in spite of the large excess of hydrogen present. This corrosion was predominantly observed in the upstream portion of the foam samples and resulted in disappearing or weakening of the nickel foam.

The sample size used for the CVD tests was 10 x 12 x 23 mm. This size was dictated by the dimensions of the crush tester (1-inch diameter mandrel). Since it was difficult to achieve uniform deposition even with these small samples, it would have been even more difficult to achieve uniform depositions with the larger samples used for the Space Shuttle APU. The CVD coating program was abandoned after these difficulties became apparent.

4.5 RESINATE COATINGS

A novel method for deposition of noble metals on conductors and nonconductors alike has been developed by the Liquid Gold Division of Engelhard Industries. Organic salts of rhodium and other noble metals can be dissolved in a volatile solvent (toluene) and painted on as a thin layer. Upon heating to 700°K (800°F) in air, the organic constituents burn away and leave a coating of metal behind. Annealing may be required to improve adhesion of the coating.

This coating method has the potential of achieving uniform deposition throughout a porous sample, because it does not depend on an electric field as electroplating. It is suspected that it will lead to heavy deposits inside the hollow ligaments because it is difficult to drain all liquid from the capillary passages.

Prior to coating foam samples, a suitable dilution of the Engelhard 8826 was determined by coating flat coupons of nickel sheet metal. It was noted that the undiluted material (10% rhodium), and even a 1:5 dilution with toluene would result in flaking of the deposit upon heating in air. A uniform deposit was achieved by diluting the material to 1 percent rhodium. A foam sample and nickel coupons were coated with this solution three times and then heated to 700°K (800°F) for minutes. Following the burnout, the samples were annealed in hydrogen for 1 hour at 1,255°K (1,800°F) to partially diffuse the rhodium coating into the nickel. The coating did not appear to be uniform and some cracks formed during drying and sintering were evident.

4.6 PENETRATION STUDY

The electroforming of metal foams is severely limited by the lack of penetration of the electric field into the porous foam structure. In the worst case, a line-of-sight relationship may be assumed. This

Table 4-2
SUMMARY OF SILICIDING AND BORIDING TESTS

CVD Agent	Concentration % by Volume	Temperature		Duration Minutes	Flow Rate ml/min.	Location	Weight Gain %	Remarks
		°K	°F					
SiCl ₄	5	1,366	2,000	17	120	Dogbone	0.64	Burned out
SiCl ₄	5	1,366	2,000	30	120	Dogbone		Burned out
SiCl ₄	1	1,073	1,472	15	120	Upstream Downstream	0.1 0.0	No post CVD heating
SiCl ₄	2	1,073	1,472	15	120	Upstream Downstream	0.0 0.0	15 min. H ₂ flow
SiCl ₄	3	1,073	1,472	30	120	Upstream Downstream Plate	4.9 4.3 0.16	14 min. H ₂ flow
SiCl ₄	3	1,073	1,472	30	240	Upstream Upstream Plate	6.7 4.9 0.55	15 min. H ₂ flow
SiCl ₄	3	1,373	2,012	15	240	Upstream Upstream Plate	10.7 14.7 0.6	Rapid cooldown, no diffusion heating
BCl ₃	3	1,273	1,832	30	240	Foam Plate	1.1	Upstream end of nickel foam heavily corroded
BCl ₃	3	1,273	1,832	90	240	Upstream Upstream	0.9 1.3	
BCl ₃	3	1,273	1,832	180	240	Upstream Upstream	2.0 2.3	

means that cathode (workpiece) areas shaded from direct view of the anodes will receive none or little metal. Fortunately, the field lines are not straight such as light beams, but follow curved patterns inside the foam structure. It is due to this fact, that foams can be prepared by electroplating at all. However, frequently a density gradient is observed from the periphery to the core of a foam sample. This density gradient is undesirable because it will cause foam samples of varying properties depending on where the raw foam piece is cut to be machined to size. In particular, during machining the outer, valuable, more dense layers are removed and the ultimate foam shape is cut from the relatively soft core.

In order to minimize sample-to-sample variations and waste of materials, it is necessary to improve the penetration capability of the electroplating process. Penetration capability is also referred to as "throwing power" in plater's jargon. No data were published to date on the effect of plating conditions on penetration in foam. Lack of penetration is recognized to be an industry-wide problem as indicated by the fact that commercial foam suppliers do not offer metal foam in thicknesses exceeding 38 mm (1.5 inch). It is very difficult to scale up a foam manufacturing to dimensions of this order of magnitude.

The variables which determine penetration are: foam pore size, foam density, type of metal to be electroplated, electrolyte concentration, mode of agitation, type and amount of plating additives, current type and current density. Only three of these variables were studied in an evaluation matrix (Table 4-3) to arrive at optimum plating conditions. Foam pore size and foam density were fixed by assignment at the beginning of the program to be nominal 20 pore/inch and 3 percent density. The metal to be plated was nickel and it may be assumed that the fundamental trends discovered in this study are valid for other metals as well. Electrolyte concentration was one of the variables studied at four different levels, as shown in Table 4-3. The mode of agitation was by recirculation pump and the liquid flow was from the workpiece toward the anode. One test was conducted with ultrasonic agitation. No plating additives were tested during this program because most brightening additives contain sulfur. Sulfur contamination must be avoided.

The main variable was found to be current density expressed in amperes/unit area. The area to which this current density relates can be expressed in two different ways: based on the outer surface area (assuming the foam sample is a solid piece of material), or based on the true surface area. The true surface area of the foam is not readily accessible by direct measurement. For this reason the outer surface area directly exposed to the anode has been used for comparison purposes. This is allowable as long as the same pore size foam is used throughout the test series. In addition to steady-state direct current, a few tests were also conducted with intermittent direct current.

The effects of ultrasonic agitation or intermittent DC were studied at nominal operating conditions. The samples were 45 mm (1.75 inch) diameter by 31 mm (1.25 inch) length cylinders held in a cylindrical sleeve such that only one flat side was exposed to the anode. The anode to cylinder cross-section area ratio was 4:1. The cylindrical sleeve extended above the electrolyte level to avoid plating of the cylinder from the rear. Electrolyte was pumped into the sleeve with a peristaltic recirculation pump.

Table 4-3
TEST MATRIX FOR PENETRATION STUDY

Electrolyte Concentration, % of Nominal Concentration \ Current Density, % of Nominal	100	50	10
200	DC* (#20)		
100	<div style="border: 1px solid black; display: inline-block; padding: 2px;">DC (#1)</div> IDC ** (#10) USA*** (#30)	DC (#2)	DC (#3 and #40)
75	DC (#4)	DC (#5)	DC (#6)
50	DC (#7)		

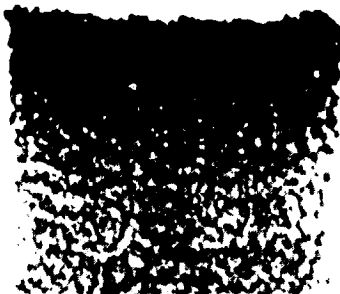





*DC = Direct current = Nominal condition
 **IDC = Intermittent direct current
 ***USA = Ultrasonic agitation

Numbers in parentheses indicate sample number in Figure 4-3.

All samples were plated to achieve a weight gain of approximately 2.2 grams. After plating, rinsing, and drying, the samples were weighed and X-rayed in a direction normal to the direction of the electric field. The X-ray shadowgraphs are mounted in Figure 4-3 in approximately the same configuration as shown in Table 4-3.

As shown in the top row, starting with the nominal plating condition at the upper left, an improvement in penetration can be achieved by reducing the current density by one order of magnitude. Even though this causes some inconvenience because plating time exceeds 20 hours, a significant improvement in uniformity of density makes the extra effort worthwhile. As a result of this matrix study, plating conditions for ("unimproved") nickel hemicylinders for Space Shuttle APU have been changed to the lower current density and improved penetration. Reducing the electrolyte concentration to 75 and 50 percent of the nominal concentration had the opposite effect. In addition, at 50 percent, the electroless plating became severely corroded and resulted in holes in the plating. Doubling the electrolyte concentration did not show a measurable improvement. Plating a sample at nominal conditions with intermittent DC (1 second pulse, 50 percent on), or with ultrasonic agitation did not result in visible improvements of penetration. Plating with ultrasonic agitation may result in an improvement of plating on a microscopic scale (reduced porosity of ligament walls), as demonstrated in Reference 11. However, this beneficial effect is subject to further study.

NICKEL ELECTROPLATING PENETRATION STUDY - X-RAY SHADOWGRAPHS

Electrolyte Concentration % of Nominal Concentration	Current Density, % of Nominal	
	100	50
100	1 NI 	2 
75	4 	5 
		6 
		40 

5.0 EVALUATION OF IMPROVED FOAMS

The new metal foams prepared during this program were evaluated in a series of laboratory tests designed to simulate reactor conditions. The exposed samples were then inspected under the metallurgical microscope and tested for crush strength. The preferred evaluation test was a 1,366°K (2,000°F), 100-hour nitridation test under ammonia. As previously shown in paragraph 3.1, there was no difference in the effects if this test was conducted with ammonia or with hydrazine. The use of ammonia was preferred for experimental reasons.

It would have been desirable to include the attrition test for foam evaluation. However, this test was not severe enough and even with the unimproved foam hardly any damage could be observed. Furthermore, this test cannot be scaled down to use the smaller samples of the foam development program.

5.1 NITRIDATION TESTS

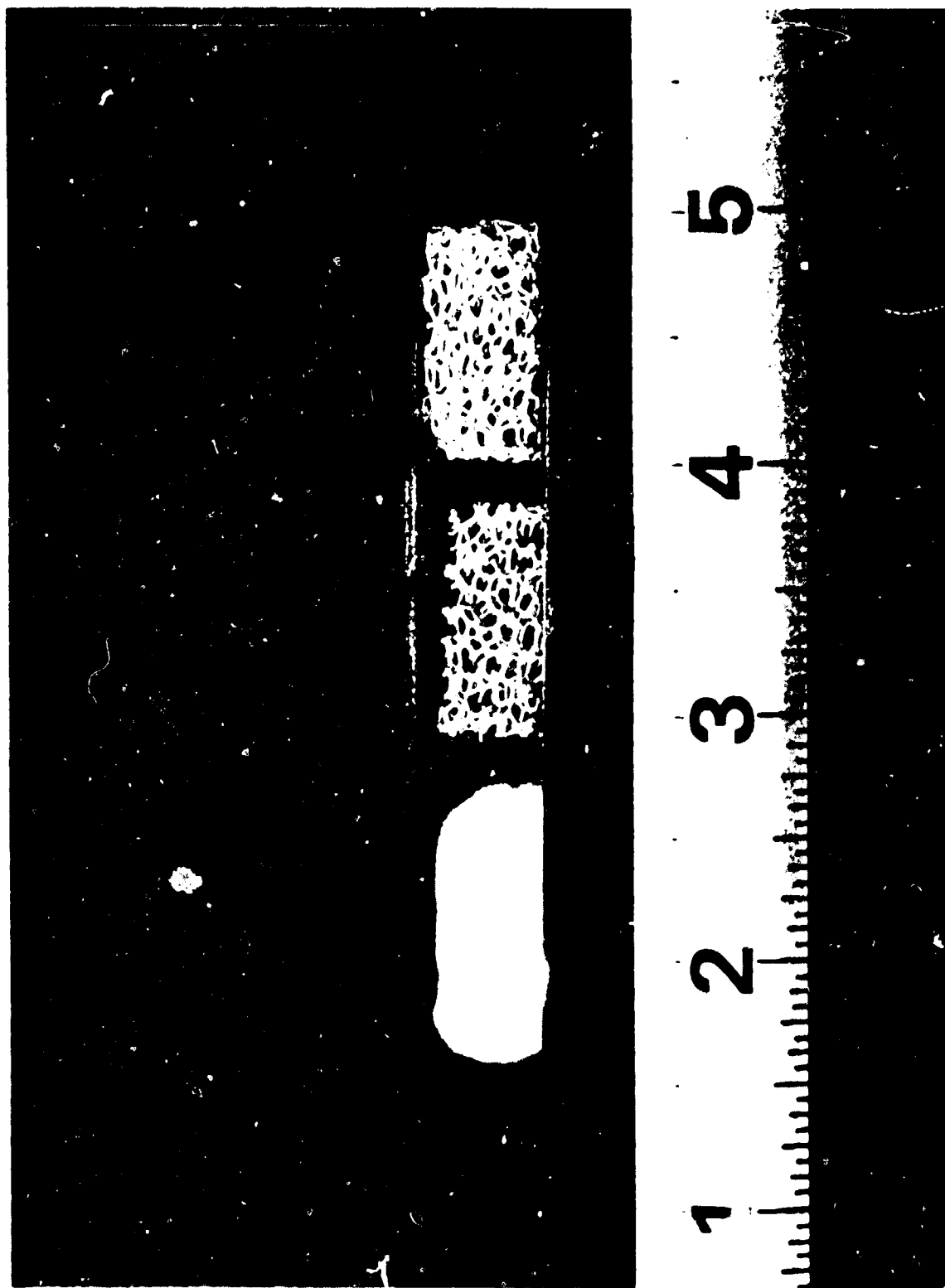
A series of nitridation tests was conducted using "standard" nickel foam as a baseline. The first test included bare nickel foam, rhodium-coated nickel foam, and all-platinum foam. Surprisingly, after 100 hours at 1,366°K (2,000°F) in flowing ammonia, the platinum foam piece had melted. Subsequently, several tests were conducted to investigate this "platinum melting phenomenon." All doubts concerning the purity of the platinum were eliminated by the fact that the same piece of platinum foam had been previously heated to 1,973°K (3,092°F) for one hour in a high temperature vacuum furnace without melting.

In the first test, rhodium-coated nickel and bare nickel foam survived the test without changes in visual appearance. The area where the platinum foam had contacted the quartz tube showed signs of severe attack. It was suspected that the melting was the result of silica from the quartz tube becoming reduced to silicon. Silicon would mix with the platinum to form a low-melting alloy. However, at least 20 percent silicon would be required to lower the melting point below 2,000°F.

In subsequent tests, the samples were therefore placed in alumina boats which are more inert than the quartz tube. Furthermore, each sample was instrumented with an individual thermocouple and temperatures of all samples were recorded throughout the test. It was suspected that platinum could heat beyond the furnace temperature by catalytic recombination of hydrogen atoms on its surface. However, no temperature excursions of the platinum pieces were recorded in any of the tests. Yet, the platinum had melted at this unusually low temperature.

Post-test inspection of the foam samples contained in the alumina boat revealed that the nickel and rhodium/nickel/rhodium foams remained visually unchanged, whereas the platinum foam had melted and the molten platinum had wicked into the porous surface of the unglazed alumina boat, creating a shiny area (Figure 5-1). The test was then repeated with a new platinum foam sample

NICKEL FOAM (RIGHT), RHODIUM/NICKEL/RHODIUM FOAM (CENTER) AND REMAINS OF PLATINUM FOAM IN ALUMINA BOAT, FOLLOWING 100-HOUR NITRIDATION TEST 1 INCH SCALE



from a different lot number; the results were identical to those of the previous test. The test was repeated with platinum foam placed on Shell 405 catalyst in an alumina boat. Again, the platinum melted partially and wicked into the Shell 405 granules.

The test without Shell 405 was then repeated under hydrogen instead of ammonia. After 100 hours at 1,366°K (2,000°F), the platinum foam had sagged and changed its structure significantly, an indication that it must have been very soft. Shiny marks were left on the alumina boat where the sample had contacted it. Also there was a sign of incipient melting. Throughout all these tests, the nickel, rhodium, and nickel/rhodium foam remained unchanged.

The cause for the platinum melting phenomenon has not yet been clearly identified. In consulting the literature, only vague recommendations could be found stating that platinum should not be exposed to reducing conditions. Trace amounts of silicon in the alumina boat and in Shell 405 are suspected to contribute to this phenomenon.

A similar platinum melting phenomenon has been previously observed during nitridation tests conducted by RRC for the Rocketdyne Division of Rockwell International (References 8 and 9). A sample of platinum wire had melted after 100 hours at 1,255°K (1,800°F). No further investigations were conducted at that time to explain this unusual reaction.

Tests conducted by Bell Aerospace under Contract F04611-73-C-0644 (Reference 12) included platinum - 10 percent rhodium coupons exposure to hydrazine exhaust "in vitro." The wrought material became softer (annealed) in the exposure, but no damaging was observed. It was concluded that platinum - 10 percent rhodium is an acceptable material, but pure platinum was not tested. Also, the test temperature was below 1,366°K and the duration was less than 100 hours.

5.2 METALLURGICAL INVESTIGATION

Figure 5-2 shows the cross-section of a rhodium/nickel/rhodium foam in the as-plated condition prior to burn out. The sample has been polished and etched to reveal the boundaries of the individual layers. The nickel assumed a granular structure, whereas the rhodium remained shiny. The shiny, more reflective rhodium layers on the inside and the outside of the ligament walls are clearly visible. Measurements with higher magnification indicated that the ligament wall is coated with approximately 160 μ m (400 μ inch) rhodium on either side. This rhodium deposit is significantly thicker than rhodium coatings commonly applied for decorative or protective purposes, such as on switches or relays. This explains why adherence problems and stress buildup problems are encountered when electroforming parts by electrodeposition from a rhodium plating bath which is designed for much thinner deposits.

CROSS-SECTION OF
RHODIUM/NICKEL/RHODIUM FOAM, ETCHED, 40X



Figure 5-3 shows a rhodium/nickel/rhodium foam after 100 hours nitriding in ammonia at 1,366°K. Comparing this photomicrograph to that of bare nickel, Figure 5-4, it is obvious that less changes have occurred in the improved foam than in the bare nickel foam. The bare nickel foam shows large voids which are larger than those shown in Figure 3-1C. It must be assumed that this void/porosity formation is one of the causes for the loss of crush strength. Etched specimens revealed excessive nitridation along the grain boundaries. The etching of the specimen in Figure 5-3 did not reveal a nickel/rhodium boundary as shown in Figure 5-2. Apparently the rhodium and nickel had diffused into each other because they form solid solutions over the entire range of compositions.

5.3 CRUSH TESTS

Not only was the initial crush strength of the rhodium-coated nickel foam significantly higher than that of bare nickel foam, but it also remained essentially unchanged as the result of nitridation test (Figure 5-5). This is the most important result of the improved foam evaluation conducted under this contract. The crush strength of sample 002-4-1 remained essentially unchanged as the result of the 100-hour nitridation test in ammonia at 1,366°K (2,000°F). The same results have been obtained with a similar sample (002-4-3) after only 8 hours of nitridation at 1,366°K. The yield point before and after was at 9 N/cm². One sample (AA-1) was significantly stronger and yielded only at almost twice the load, 16 N/cm².

It is suspected that some of the sample-to-sample variation of crush strength is caused by the anisotropy of the original open-cell foam. The foam cells are not truly spherical (dodecahedral), but ellipsoidal. The crush strength is expected to differ depending on the direction in which the load is applied. The orientation of the cells was not always recorded when crush tests were performed. However, the tests were of sufficient repeatability to demonstrate that the rhodium-nickel foam had higher crush strength than the bare nickel foam.

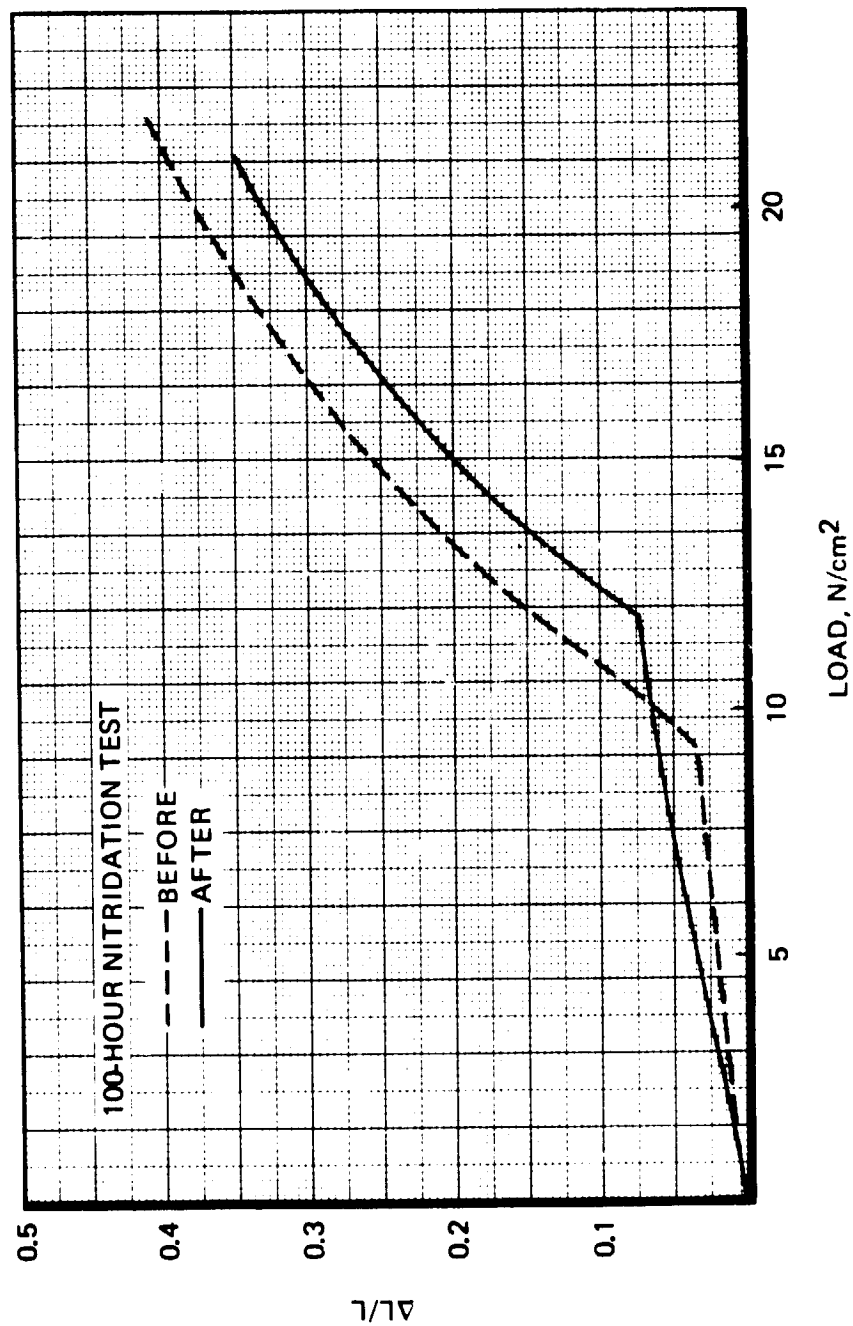
Figure 5-3
RHODIUM/NICKEL/RHODIUM FOAM
AFTER 100-HOURS NITRIDATION IN AMMONIA
AT 1,366°K. 160X, UNETCHED



Figure 5-4
BARE NICKEL FOAM
AFTER 100-HOURS NITRIDATION IN AMMONIA
AT 1,366°K. 160X, UNETCHED



CRUSH STRENGTH OF RHODIUM-NICKEL-RHODIUM FOAM (002-4-1)
BEFORE AND AFTER NITRIDATION TEST



6.0 CONCLUSIONS AND RECOMMENDATIONS

Analysis and inspection of nickel foam samples removed from monopropellant hydrazine reactors has revealed insufficient strength of the metal ligaments as the cause for nickel foam degradation. The lack of mechanical strength, which is documented by collapsed, flattened and rounded ligaments, is aggravated by a progressive loss of ductility due to nitridation. Additionally, the abrasive action of moving catalyst particles accelerates the deterioration of the foam. An attempt has been made to reproduce the nickel foam degradation mechanism under laboratory conditions, but the reactor mode of degradation could not be totally simulated.

A rhodium-coated nickel foam was found to be the most promising improved foam developed under this program. Platinum foam was eliminated from further consideration due to a melting problem. Attempts to prepare an all-rhodium foam were not successful due to excessive stress accumulation in the coating, which invariably resulted in cracking of the foam ligaments.

It was recommended to conduct reactor tests on the improved rhodium/nickel/rhodium foam and to scale up the manufacturing process to produce foam samples large enough for Space Shuttle APU-GG testing.

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